

REMARKS

Claims 1-17 are pending in this application. Non-elected claims 6-11 are withdrawn from consideration by the Examiner. By this Amendment, claim 17 is added. Support for the new claim may be found, for example, in the specification at page 8, lines 6-9. No new matter is added.

In view of the foregoing amendments and following remarks, reconsideration and allowance are respectfully requested.

I. Rejections Under 35 U.S.C. §103**A. Shue and the Merriam-Webster Online Dictionary**

The Office Action rejects claims 1-5 and 12-16 under 35 U.S.C. §103(a) over U.S. Patent No. 4,489,129 to Shue et al. (hereinafter "Shue") and the Merriam-Webster Online Dictionary (hereinafter "the dictionary"). Applicants respectfully traverse the rejection.

Claim 1 is directed to a composite material and requires that "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight." Claim 13 and its dependent claims, are directed to a coated reinforcing fiber, do not mention the word "composite," and also require that "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight." Shue and the dictionary do not render obvious or establish any reason or rationale to provide such a combination of features.

Shue generally discloses polymer-coated reinforcement fibers for composite materials. See Shue, Abstract. In order to improve certain mechanical properties, such as strength, stiffness and fatigue life, the reinforcement fibers are coated with a curable polymer, such as polyphenylene sulfide (PPS). See Shue, column 1, lines 1-52. Shue indicates that for most purposes the content of the polymer ranges is from about 0.1 to about 10 wt.% relative to the total weight of the polymer and the reinforcements (an order of magnitude greater than that recited in claims 1 and 13); however, as acknowledged in the Office Action, Shue discloses

that the amount of polymer coating may vary widely. See Shue, column 3, lines 20-28 (emphasis added). Therefore, including the above guidance and the fact that Shue prefers a content range is from 6 to about 8 wt.% relative to the total weight of the polymer and the reinforcements (when the reinforcements are fibers; see Shue, column 3, lines 24-26) Shue fails to provide any guidance or reason or rationale for to one having ordinary skill in the art to achieve the combination of features recited in claims 1 and 13.

However, in view of Shue's disclosure that the amount of polymer coating may vary widely, the Office Action asserts that there is sufficient suggestion to modify the amount of polymer coating on the reinforcement. Under this unreasonably broad interpretation of Shue, Shue discloses every possible combination of the amount of polymer coating relative to the reinforcing fibers (i.e., 0 to 100%, exclusive, of the polymer coating relative to the reinforcing fiber).

Applicant's respectfully submit that the claimed range achieves unexpected results relative to the above extremely broad range of polymer coating relative to the reinforcing fibers disclosed in Shue and thus is critical, which renders the claims unobvious. As described in the present specification at paragraphs [0004] to [0006], Examples 1 and 2, and the Table (see specification, page 10), the claimed coating having PPS relative to the reinforcing fibers in a content in the claimed range produces an unexpected improvement in the apparent interlaminar shear strength ("ILSS") and of the bending strength ("BS") of the composite material containing reinforcing fibers, as compared to a composite material containing reinforcing fibers lacking a coating containing PPS.

As evidenced by the attached excerpts from: (1) J.-B. Donnet, T. K. Wang, J. C. M. Peng (editors): "Carbon Fibers," Marcel Dekker, Inc., 3rd ed., 1998, Chapters 3.8 and 3.9, pp. 210-223; and (2) J.-K. Kim, Y. -W. Mai: "Engineering Interfaces in Fiber Reinforced Composites," Elsevier, 1998, Chapter 3.3, pp. 61-66; ILSS and BS relate to the mechanical

stability at the interface between the reinforcing fiber and matrix (i.e., the fiber-matrix adhesion), not merely to any mechanical property of a composite material. ILSS and BS are tests that are used to determine the fiber-matrix adhesion. The fiber-matrix adhesion is the adhesion between the reinforcing fibers and the matrix into which the reinforcing fibers are embedded to form the composite material.

As described in the present specification at paragraphs [0004] to [0006], Examples 1 and 2, and the Table (see specification, page 10), there is a maximum PPS content at which ILSS and the BS are optimized; above this maximum PPS content, a decrease in the ILSS occurs. Thus, it is clearly demonstrated that the claimed content of PPS relative to the reinforcing fibers is critical and produces unexpected results relative to the extremely broad range disclosed in Shue. Such critical results are neither disclosed nor suggested in Shue and the dictionary and thus such evidence of unexpected results within the narrow claimed range renders the claims unobvious.

Furthermore, Applicants submit that the Office Action is relying upon impermissible hindsight by relying upon the disclosed advantages of the claims, as provided in Applicants' own specification, as a roadmap for modifying the applied references. The Office Action has no support or evidence in the applied reference or elsewhere, aside from Applicants' own disclosure, that the claimed modification would result in the unexpected improvement in the apparent ILSS and of the BS of the composite material containing reinforcing fibers, as compared to a composite material containing reinforcing fibers lacking a coating containing the recited proportion of PPS. Because one skilled in the art would not have any reason to modify the disclosure of Shue, Applicants further submit that one skilled in the art would not have been able to arrive at the claimed combination with any reasonable expectation of success by modifying the deficient teachings of the applied references.

Furthermore, Shue and the dictionary do not disclose or appreciate the unexpected results stemming from a composite material of claim 1 having "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight" and a coated reinforcing fiber of claim 13 having "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight."

For at least all of these reasons, claims 1 and 13 and the claims dependent therefrom would not have been rendered obvious by Shue and the dictionary. Accordingly, Applicants respectfully request reconsideration and withdrawal of the rejection.

B. Harris

The Office Action rejects claims 1-5 and 12-16 under 35 U.S.C. §103(a) over in view of U.S. Patent No. 4,910,289 to Harris (hereinafter "Harris"). Applicants respectfully traverse the rejection.

Claim 1 is directed to a composite material and requires that "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight." Claim 13 is directed to a coated reinforcing fiber and also requires that "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight." Harris (1) does not teach, suggest or establish any reason or rationale to provide such a combination of features, and (2) fails to provide any motivation for one of ordinary skill in the art to adjust the polyphenylene sulfide concentration relative to the reinforcing fibers, much less recognize the proportion of polyphenylene sulfide relative to the reinforcing fibers as a result-effective variable (which is required for a parameter to be optimized).

Harris discloses miscible poly(aryl ether ketone) blends that contain from about 98 to 99.9% by weight of a miscible poly(aryl ether ketone) blend, and from about 0.1 to about 2% of a poly(phenylene sulfide) (PPS). See Harris, Abstract. Thus, Harris discloses a proportion of PPS relative to the miscible poly(aryl ether ketone) blend is 0.1 to 2 percent by weight.

However, claim 1 recites the proportion of PPS relative to the reinforcing fibers. The Office Action acknowledges Harris fails to disclose that the proportion of PPS is relative to the reinforcing fibers. See Office Action, page 8. Thus, the rejection is improper at least because Harris does not disclose that the proportion of PPS is relative to the reinforcing fibers, as recited in claims 1 and 13.

Although Harris mentions in passing that the compositions may include reinforcing fibers (see Harris, column 22, lines 36-38), Harris fails to disclose what amounts of fibers may be used in its compositions, or provide any disclosure that would teach or have rendered obvious, or established any reason or rationale to provide a ratio of the weight % of PPS to reinforcing fibers, as recited in claims 1 and 13 (emphasis added).

Furthermore, Harris is concerned with a very specific problem with a specified class of miscible polymers. In other words, the disclosure of Harris is related to improved crystallization rates of PAEKs blended with a polyetherimide, certain poly(amide-imides) and/or polyimides. See Harris, column 4, lines 10-13. Harris discovered that by adding PPS to such PAEK miscible blends in an amount from about 0.1 to about 2% by weight significantly improves the crystallization rate of those specific polymer blends. See Harris, column 4, lines 8-21. Thus, Harris cannot be considered analogous art to the instant application. Accordingly, Harris cannot be reasonably considered to teach, suggest or establish any reason or rationale to provide an amount of 0.001 to < 0.01 wt% of PPS relative to the reinforcing fibers.

The Office Action asserts that it would have been obvious to one of skill in the art at the time of the invention to optimize the amount of PPS based upon the teachings of Harris. See Office Action, page 8. However, Harris does not disclose any ratio of the weight of PPS relative to the weight of reinforcing fibers or any reason to adjust the PPS concentration relative to the reinforcing fibers.

It is well settled that a particular parameter must first be recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation. *In re Antonie*, 559 F.2d 618, 195 USPQ 6 (CCPA 1977). Because Harris fails to recognize the particular parameter of "a proportion of polyphenylene sulfide relative to the reinforcing fibers," it would not have been obvious for one of skill in the art at the time of the invention to modify the teachings of Harris in the manner suggested by the Office Action and arrive at the subject matter of claims 1 and 13.

Rather, Applicants submit that the Office Action is relying upon impermissible hindsight by relying upon the disclosed advantages of the claims, as provided in Applicants' own specification, as a roadmap for modifying Harris. The Office Action has no support or evidence in the applied reference or elsewhere, aside from Applicants' own disclosure, that the claimed modification would result in the unexpected improvement in the apparent ILSS and of the BS of the composite material containing reinforcing fibers, as compared to a composite material containing reinforcing fibers lacking a coating containing the recited proportion of PPS. Because one skilled in the art would not have any reason to modify the disclosure of Harris, Applicants further submit that one skilled in the art would not have been able to arrive at the claimed combination with any reasonable expectation of success by modifying the deficient teachings of Harris.

Furthermore, Harris not disclose or appreciate the unexpected results (as discussed above) stemming from a composite material of claim 1 having "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight" and a coated reinforcing fiber of claim 13 having "a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight." For example, as described in the present specification at paragraphs [0004] to [0006], Examples 1 and 2, and

the Table (see specification, page 10), the claimed coating having PPS relative to the reinforcing fibers in a content in the claimed range produces an unexpected improvement in the apparent ILSS and of the BS of the composite material containing reinforcing fibers, as compared to a composite material containing reinforcing fibers lacking a coating containing PPS. Moreover, there is a maximum PPS content at which ILSS and the BS are optimized; above this maximum PPS content, a decrease in the ILSS occurs. Such results are neither disclosed nor suggested in Harris.

For at least these reasons, claims 1 and 13 and their dependent claims would not have been rendered obvious by Harris. Accordingly, reconsideration and withdrawal of the rejection are respectfully requested.

II. New Claim

By this Amendment, new claim 17 is presented. New claim 17 depends from claim 1 and, thus, distinguishes over the applied references for at least the reasons discussed above with respect to claim 1. Additionally, the applied references fail to disclose "a proportion of the reinforcing fibers is 40% to 70% by volume of the composite material."

Prompt examination and allowance of new claim 17 are respectfully requested.

III. Rejoinder

Applicants also respectfully request rejoinder of withdrawn claims 6-11. PCT Rule 13.1 provides that an "international application shall relate to one invention only or to a group of inventions so linked as to form a single general inventive concept." PCT Rule 13.2 states:

Where a group of inventions is claimed in one and the same international application, the requirement of unity of invention referred to in Rule 13.1 shall be fulfilled only when there is a technical relationship among those inventions involving one or more of the same or corresponding special technical features. The expression "special technical features" shall mean those technical features that define a contribution which each of the claimed inventions, considered as a whole, makes over the prior art.

Applicants respectfully submit that each of claims 1-17 share the following technical feature: coated reinforcing fibers each comprising a reinforcing fiber and a coating, the coating comprising polyphenylene sulfide, wherein a proportion of polyphenylene sulfide relative to the reinforcing fibers is 0.001 to < 0.01 percent by weight. Because there is nothing on the record that establishes that this technical feature does not define a contribution which each of the claimed inventions, considered as a whole, makes over the prior art, unity of invention exists among claims 1-17.

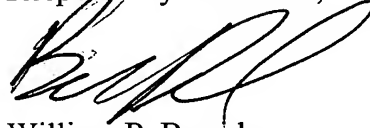
Accordingly, Applicant respectfully requests withdrawal of the restriction requirement and rejoinder of withdrawn claims 6-11.

IV. Conclusion

In view of the foregoing, it is respectfully submitted that this application is in condition for allowance. Favorable reconsideration and prompt allowance of this application are earnestly solicited.

Should the Examiner believe that anything further would be desirable in order to place this application in even better condition for allowance, the Examiner is invited to contact the undersigned at the telephone number set forth below.

Respectfully submitted,



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Date: August 21, 2009

Attachments:

J.-B. Donnet, T. K. Wang, J. C. M. Peng (editors): "Carbon Fibers;" Marcel Dekker, Inc., 3rd ed., 1998, Chapters 3.8 and 3.9, pp. 210-223.

J.-K. Kim, Y. -W. Mai: "Engineering Interfaces in Fiber Reinforced Composites," Elsevier, 1998, Chapter 3.3, pp. 61-66.

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CARBON FIBERS

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PREFACE

Carbon fiber, commercially available since the 1960s, has attracted worldwide interest as a high-performance material. With its light weight and excellent engineering properties, in the form of high modulus and high strength fiber materials it was initially developed for aircraft and aerospace use.

Despite initially high expectations and the remarkable scientific and technical fertility of the domain where we have seen the introduction of cellulosic, PAN, pitch and mesophase pitch fibers, and more recently vapor grown fibers, each of them initiating an impressive development, the commercial success was not immediate and it experienced successive up and downs.

The 1970s prediction of a world market rapidly growing to 10,000 tons/yr was not fulfilled until 1995. These commercial difficulties resulted in an ever changing scene, with constant spin-offs of industrial companies and first class chemical groups going into production, development, and marketing, then leaving it, sometimes temporarily, to newcomers. The market is now expanding and, despite the reduction of the military market in recent years, the success of the civil aerospace, recreation and other applications have helped sustain a world market of 12,500 tons/yr in 1997, with forecasts to reach 50,000 tons/yr in the next five to ten years.

In the past eight years an enormous amount of new information on carbon fibers has been produced, expanding the existing literature from the time of the first edition (1984) and the revised second edition (1989) of *Carbon Fibers*.

3.8 SIZING OF CARBON FIBERS

In the manufacturing process, carbon fibers are usually coated with a very thin layer of epoxy resin or so-called "matrix-compatible sizings" after the proprietary surface treatments. These sizings are applied to carbon fibers for the protection of possible damage during transportation or handling. Carbon fibers are brittle materials and are therefore susceptible to strength degradation due to the presence of surface flaws. It is believed that the fiber sizing is beneficial because it prevents fiber to fiber contact and hence the introduction of surface flaws. Other advantages are to improve the wetting ability of the fiber by the matrix, as well as to prevent the surface reactivity by blocking the surface functional groups [116]. From the composite manufacturing viewpoint, complete and thorough wetting of the tows with several thousand filaments is a necessary condition for good composite properties. The application of a matrix compatible finish could enhance wetting of the fibers by the matrix and therefore improve the interfacial shear strength.

Drzal *et al.* [116] examined the effect of the sizings on the fiber-matrix adhesion. The authors used the embedded single-fiber critical length test to measure the effect on adhesion of surface-treated carbon fibers which were coated with 100 nm epoxy resin (without curing agent), and found the interfacial shear strength increase by about 25%. Drzal [117] proposed that the sizing layer interacts with the bulk matrix and causes a change in local properties in the fiber-matrix interphase. The properties of this sizing layer itself are imparted to the interphase and can affect adhesion. They suggested [116] mechanisms for the function of sizing on the adhesion of carbon fiber composites. First of all, application of a fiber sizing could contribute to fiber-matrix adhesion through the creation of a protective environment for the reactive surface groups which were added to the fiber surface with treatment. Secondly, the failure mode was changed from an interfacial crack propagation to a matrix crack growth perpendicular to the fiber axis. Yumitori *et al.* [121] reached a similar conclusion from their study on the role of sizing resin in carbon fiber-reinforced poly(ether sulfone) composites. Sized carbon fibers show a higher interfacial shear strength than the unsized ones. They suggested from the analysis of time-of-flight secondary ion mass spectrometry that this adhesion enhancement arises from a strong interaction between sizing resin, the fiber and the matrix.

Sherwood *et al.* [118] studied the effect of sizings on PAN and pitch-based carbon fibers by XPS, scanning electron and x-ray wavelength dispersive microscopies. A sizing compound, bisphenol A epoxy resin, was added to the carbon fibers were previously subjected to various levels of surface treatment. By using solvents or heat-treatment to remove the size from the fiber surface, they examined the size compounds on the effect of adhesion. The surface.

chemistry of the sized fibers was dominated by the sizing and also more sizing compounds were found on the fibers which received greater prior surface treatment. They claimed that some remarkable interaction probably occurs between the size and the surface treated fiber, and this interaction leads to a greater stability of the size on the fiber surface. Sizing resin structure and interphase formation in carbon fiber composites were investigated by Anderson *et al.* [119]. The presence of a sizing resin on the as-received fibers reduced the interfacial shear strength of the composite. They suggested that compatibility of the deposited size with the matrix determines the adhesive bond between fiber and matrix and the formation of an interfacial region. On the other hand, deposition of a sizing resin from solution led to a different conclusion that chemical interaction with the fiber surface had occurred. During composite fabrication these sizing resins will therefore have to act as "coupling agents" with the matrix. Solvent extension of emulsion-deposited sizing resins, particularly at elevated temperatures, appeared to promote their interaction with the fiber surface. Wu and his co-workers [122] also discovered that the sizing treatment of carbon fiber has a great effect on the properties of 3D C/C composites. Furfuryl alcohol-maleic-anhydride-ethylene-glycol resin was found to be one of the best sizing agents because of its ability to form a firm layer to protect fiber from attack by a matrix precursor. The sizing improves the mechanical properties of 3D C/C composites, in particular the toughness and flexural strength. An almost two-fold increase of flexural strength has been obtained by this process.

Sato and Kurauchi studied the effect of fiber sizing on composite interfacial deformation by thermo-acoustic emission measurement [120]. The system was run by heating the furnace to 200°C at a rate of 2°C min⁻¹ and then to cool to room temperature at the same rate. The acoustic emission from the specimen under the thermal cycle was detected by a transducer. Figure 31 shows the change of the emission activity with increasing fiber sizing. The acoustic emission was hardly observed during heating, whereas a lot of emission was observed during cooling, particularly below the glass transition temperature of the matrix resin (140°C). The thermo-acoustic emission activity was found to decrease dramatically with the increase of sizing. Accordingly, the mechanical properties of the composites with different sizings are listed in Table 10 where the samples were evaluated by a bend test at room temperature and 120°C, respectively. The tested composite is a randomly dispersed short carbon fiber-resin reinforced sheet-moulding compound made by hot-compression moulding under 10 MPa at 140°C for 10 min. The matrix was a modified vinyl ester resin and the volume fraction of the fiber for the composites was 40%. As shown, the bending modulus and bending strength decreased with the increase of sizing, particularly at 120°C.

Possible reasons were proposed by the authors to explain the change of the emission activity and mechanical properties. A larger sizing generates a thicker interphase which acts as a buffer layer for the stress transformation. The generated thermal stress concentration is relaxed through the interphase when the composite is subjected to a thermal cycle. A thicker interphase can prevent the thermal cracking because it provides a larger relaxation. That is the reason why the emission activity decreased with an increase in the sizing. In contrast, when the composite is subjected to an external load the efficiency of stress transfer from the matrix to the fiber is decreased by the presence of a thicker interphase, therefore the bending strength decreases.

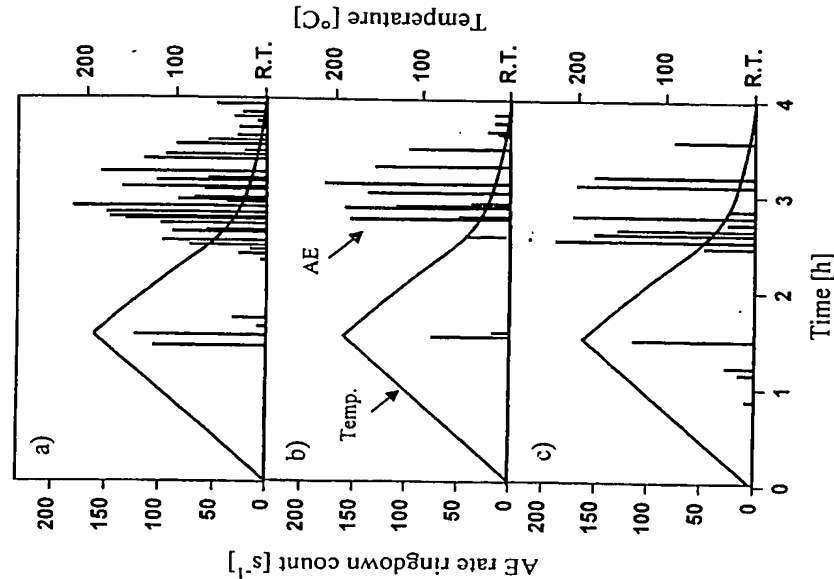


Figure 31 Thermo-acoustic emission behavior of the specimens, showing the decrease of the emission activity with the increase in the fiber sizing. AE, Acoustic emission; R.T., room temperature. Sizing (a) 0.2%, (b) 1% and (c) 3% [120] (Reprinted with permission from Chapman & Hall).

Table 10 Change of the Mechanical Properties of the Specimens with Increasing Fiber Sizing

	Room temperature		120°C	
	Bending modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)	Bending strength (MPa)
Sizing 0.2%	35	410	23	170
Sizing 1%	35	310	16	110
Sizing 3%	28	270	8.0	46

Source: from ref. 120. (Reprinted with permission from Chapman & Hall.)

3.9 Influence of Surface Treatments on Carbon Fiber Composite Properties

Carbon fiber composite properties could be affected by the surface treatment in the fiber direction. Two effects play an important role in the longitudinal tensile strength. First, the carbon fiber surface treatment has some influence on the individual fiber strength. Secondly, an improved interface strength leads to better load transfer in the composite. The effect of surface treatments and fiber sizings on the stress transfer characteristics and composite properties of AS-4 carbon fiber/epoxy composites were evaluated by Okhuysen et al. [123]. Fiber surface functional groups were experimentally varied from acidic to basic with RF glow discharge plasmas of CO_2 and NH_3 and the products were characterized by XPS techniques. Sizings composed of diglycidyl ether of bisphenol-A (DGEBA) were applied to some of the treated fibers. The interfacial shear strength of carbon fiber composites made with DGEBA/*m*-phenylene diamine resin was measured by the single fiber tension tests. Short beam shear and transverse flexural tests were used to examine the composite properties of modified materials. Results showed that the surface chemistry of the fiber was efficiently affected by the plasma treatments but the changes had surprisingly little effect on the critical stress transfer length. Transverse flexural tests were more sensitive to the changes in surface characteristics, however, the interlaminar shear strength of the composites were unaffected by the treatments.

Blackketter et al. [124] examined the surface treatment on the transverse tensile and shear strengths of carbon fiber-reinforced thermoset and thermoplastic matrix composites. The mechanical properties of high

performance composites depend extensively on the adhesion of fiber and matrix. It is particularly true for maximizing the strength of unidirectional composites in off-axis directions. The composites were made by PAN-based carbon fibers (XA and A4) with EPON 828 epoxy (thermoset) and liquid crystal polymer (LCP, thermoplastic) matrix compounds. Four types of XA fibers were studied, untreated and treated fibers without sizing (XAU & XAS), and with sizing levels of 0.7% (XA-C1) and 1.2% (XA-C2), all in 12K filament tows. The A4 fibers were supplied in 6K tows, of which untreated (AU4), treated but unsized (AS4), and treated with an epoxy sizing (AS4-C) were studied. The influence of surface treatment was investigated by measuring the transverse flexural tensile (TF) and the short-beam shear (SBS) strengths of unidirectional composites. The shear and transverse tensile strengths illustrated in Table 11 were improved by the surface treatment for both the thermoset and thermoplastic reinforced fiber composites.

Table 11 Fiber Volume, Short Beam Shear (SBS) Strength, Transverse Flexural (TF) Strength, and the Ratio of SBS to TF Strength

	Fiber volume (%)	SBS strength (MPa)	TF strength (MPa)	Ratio SBS/TF
AU4/EPON 828	59	39.6	29.6	1.34
AS4/EPON 828	61	71.2	39.7	1.80
AS4-C/EPON 828	62	73.1	78.2	0.94
XAU/EPON 828	57	65.0	40.0	1.63
XAU-C1/EPON 828	55	59.3	41.0	1.45
XAU-C2/EPON 828	61	67.0	38.0	1.76
XAS/EPON 828	55	73.0	63.0	1.16
XAS-C1/EPON 828	55	80.0	77.0	1.04
XAS-C2/EPON 828	55	75.0	64.0	1.17
AS4/LCP	60	49.0	43.7	1.12
XAU/LCP	60	39.6	43.2	0.92
XAS/LCP	61	51.9	56.8	0.91

Source: from ref. 124. (Reprinted with the permission from Society of Plastics Engineers.)

Peng and Buttry [133,134] have recently proposed a possible mechanism of producing good adhesion in the carbon fiber/epoxy composite system which involve the attack of amine groups as nucleophiles from the hardener directly at non-oxygen-containing reactive sites at the carbon fiber surface. As illustrated in Figure 32, they proposed that a Michael-like reaction [135,136] might occur on the carbon fiber surface in which amine groups as nucleophiles and the vinylic C = C bonds at the carbon fiber surface act as electrophiles. In support of this proposal, they selected a variety of N-alkylamines to thermally react with carbon fibers. This means of manipulating adhesion is schematically presented in Figure 33. In the case of reaction A, an interfacial immobilization of simple N-alkylamines, if the amine immobilized species consume most of the reactive sites at the carbon fiber surface, then the interfacial layer will not have enough functionalities to react with epoxy resins to produce good adhesion. On the other hand, reaction B gives an example of interfacial immobilization of a reagent which could offer a direct chemical bonding between the fiber surface and the matrix, and the adhesion is predicted to be improved relative to the case for reaction A. A set of Tonen HMU (high modulus untreated) pitch-based carbon fibers were reacted with didecylamine, dodecylamine, 1,6-diaminohexane, and 1,9-diaminononane, respectively, at 180°C for 15 hours under the same reaction conditions. Then, the amine treated fibers were mixed with EPON828-mPDA epoxy resin for the embedded single fiber tests to measure the amine immobilization effect on the interfacial shear strength between fiber and matrix. The apparent fiber-matrix interfacial shear strength, τ_y , was measured at 83, 59, 21, 29, and 28 MPa for Tonen HMU + 1,9-diaminononane, Tonen HMU + 1,6-diaminohexane, Tonen + didecylamine, Tonen + dodecylamine, and Tonen HMU samples, respectively. As expected, the interfacial shear strength of the 1,9-diaminononane or 1,6-diaminohexane immobilized fiber shows $\geq 100\%$ improvement over the control sample, presumably due to the chemical bonding between the free end of the immobilized amines and the epoxy groups in the resin. For the didecylamine sample, the authors speculated that the long alkyl chains of didecylamine blocked some of the resin molecules from reacting with carbon fiber, leading to a poor interfacial shear strength, about 22% less than that of the HMU control experiments.

When sizing was applied to the fibers after surface treatment, there was an additional improvement in the SBS and TF strengths for all the fiber/epoxy composites. Also, the TF strength was improved to a greater degree than the SBS strength by the surface treatment and sizing. Furthermore, TF strength appeared to be more sensitive to sizing than the SBS strength. The low sensitivity of the SBS strength could be explained by the fact that the shear failure mode is more dependent on friction or mechanical interlocking between

for XA fibers in the epoxy systems with respect to sizing level effect on the properties, the 0.7% level seems to be a better approach than the 1.2% level. Possible reasons for the observed difference could be a reduced effect of mechanical interlocking or the lack of hardener in the interface region [126] for the higher level of sizing. Drzal et al. [126] suggested that the interface becomes more brittle as the sizing levels increase, and therefore the hardener molecules are more difficult to penetrate the sizing layer.

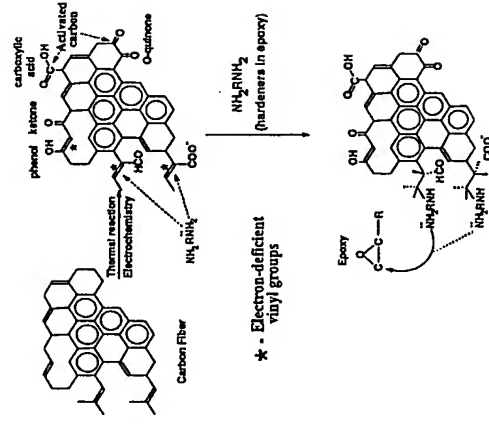


Figure 32 A proposed mechanism of nucleophilic reaction of amine compounds with vinylic groups at the carbon fiber surface [133].

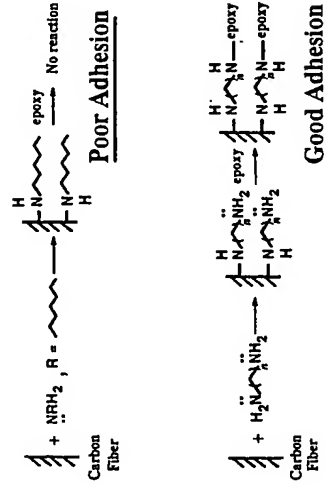


Figure 33 Schematic presentation of N-alkylamines as adhesion controlling reagents to manipulate the interfacial adhesion in carbon fiber/epoxy composites [133].

The effect of surface treatment was investigated on pitch-based carbon fiber composites reinforced with engineering thermoplastic resin-polyethersulfone, possessing high heat and chemical resistance [125]. Both nitric acid (60%) and hydrogen peroxide (15%) solutions were used as oxidizing agents to treat fibers at 60°C for different lengths of time (12 and 24 h). The effect of the fiber oxidative treatment on the interlaminar shear strength (ILSS) is presented in Figure 34 [125]. The ILSS values of the oxidative treated fibers were about two times greater than that of the untreated CF. It is evident that the surface treatment in nitric acid and hydrogen peroxide solutions on the carbon fiber/polyethersulfone powder-impregnated composite (IPCF) is effective to improving the interlaminar shear strength. As seen in Figure 35, the oxidative treatment on IPCF resulted in an increase in the transverse flexural strength as well as in the ILSS. On the other hand, the longitudinal flexural strength of the oxidative treated IPCF composite varied slightly compared with the untreated samples. The composite prepared after a 60% nitric acid solution 24 h treatment illustrated slightly lower strength than composites from the other two treatments. It was thought that the strong bonding between fiber and matrix molecules, of which the nitric acid 24 h treated samples had the highest values of both the ILSS and the transverse flexural strength, caused the decrease of the longitudinal flexural strength.

The effect of varied wet oxidation treatments (68% HNO₃, 110°C, 10 min–150 h) of high modulus fibers on the properties of the fiber and on the properties of carbon fiber-epoxy composites are presented in Figure 36 [127]. It is evident that the surface oxides and the BET surface area are increased after oxidation. However, the fiber tensile strength is decreased because of the oxidative degradation. Both the surface oxides and surface area affect the mechanical properties of composites. The observed slow BET increase could hardly be correlated with the steep improvement of ILSS and flexural strength after a short-time (< 24 h) oxidation of fibers. Instead, the increasing amount of surface oxides could better explain the improvement of ILSS. The improvement of the adhesion with continued oxidation treatment is illustrated by the translation of the fiber strength into the composite. This translation relates to the values of fiber strength after the oxidation treatment [127]:

$$\eta = \tau_b / \chi_F \tau_{z,F}$$

Where $\tau_{z,F}$ is the fiber tensile strength, τ_b is the composite flexural strength and χ_F is the fiber volume content. The translation of the fiber strength is further limited after a short oxidation time. This indicates that increased oxidation by the extended treatment produces an overoxidizing effect which strongly influences the fracture behavior.

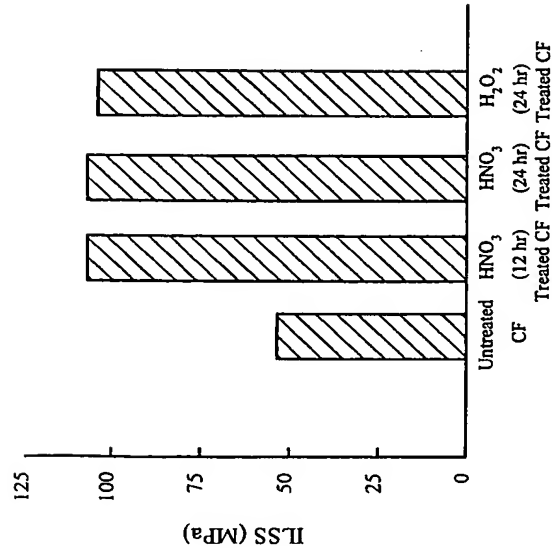


Figure 34 Interlaminar shear strength and surface treatment conditions [125]. (Reprinted with permission from Society of Plastics Engineers.)

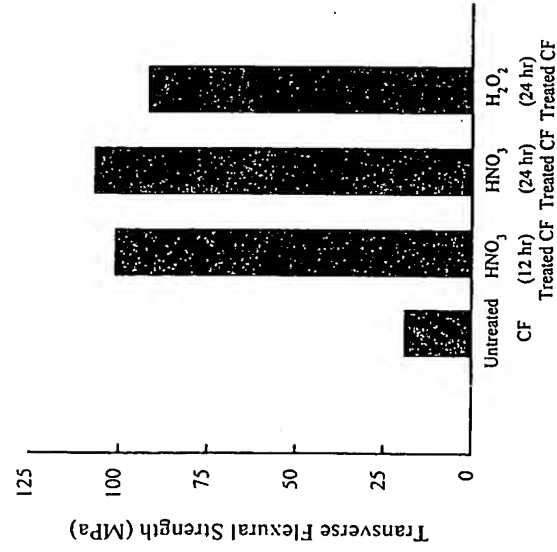


Figure 35 Transverse flexural strength and surface treatment conditions [125]. (Reprinted with permission from Society of Plastics Engineers.)

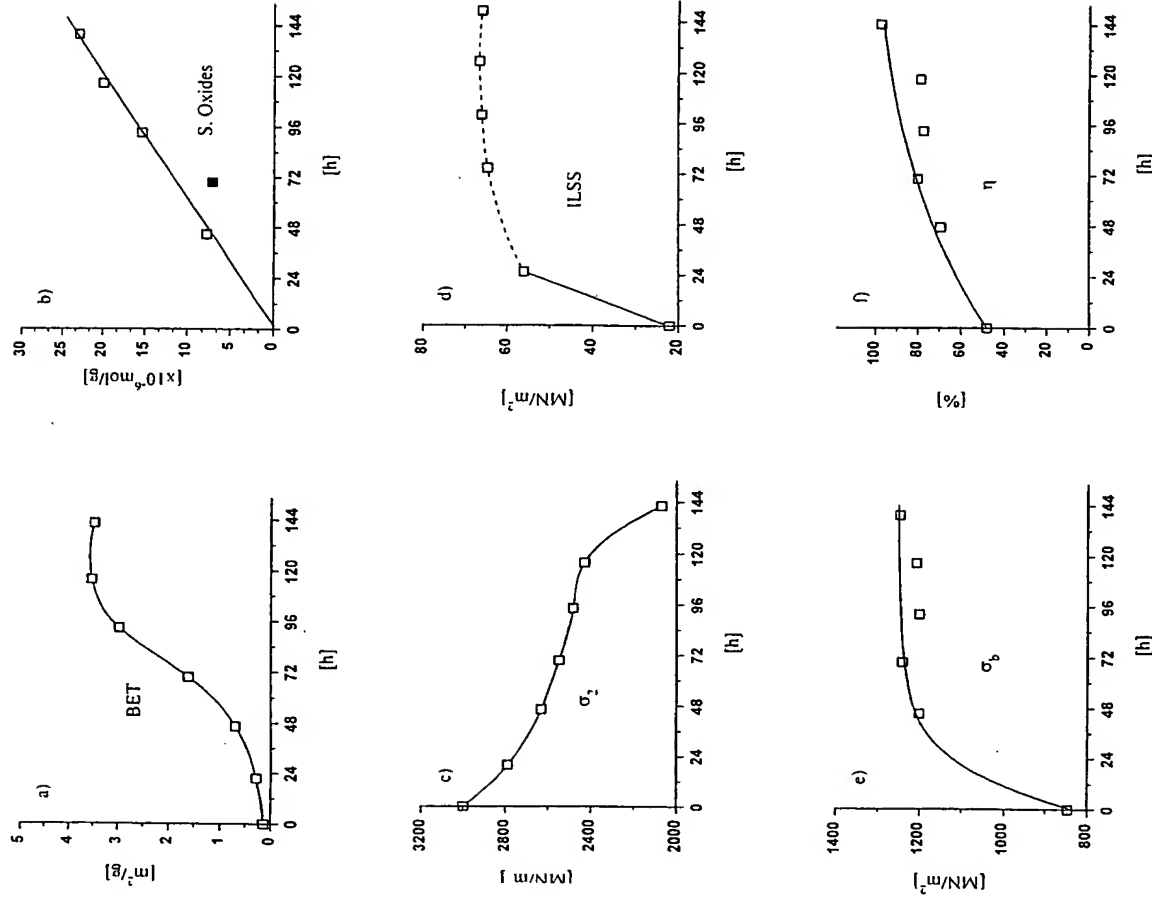


Figure 36 Influence of the wet oxidation procedure of Sigrafil HM carbon fibers on fiber and composite properties. Fiber properties: (a) BET surface area, (b) amount of surface oxides and (c) tensile strength (σ₂) of C-fibers. Composite properties: (d) Interlaminar shear strength (ILSS), (e) flexural strength and (f) translation of fiber properties into the composite (η) [127]. (Reprinted with permission from Elsevier Science, Ltd.)

Drzal and Madhukar [128] comprehensively discussed the relationship between the fiber-matrix adhesion and its composite mechanical properties. Three types of PAN-based fibers, untreated (AU4), surface treated (AS4), and surface treated with sizing were studied. Average values of the on-axis and off-axis properties for the three composite systems are listed in Table 12 and Table 13. A discussion on the results is provided below. The composite 0° tensile strength is proportional to the interfacial shear strength in the intermediate region. If the interfacial strength is too weak, the composite fails too soon due to a cumulative weakening of the material. However, the failure mode shifts from interfacial to matrix and the composite becomes more brittle when the interfacial bond strength is excessive. Composite compressive strength is enhanced by increasing the fiber-matrix adhesion. However, when the ISS was increased from low to intermediate values the flexural properties in the longitudinal are little affected. In regard to the off-axis properties, the transverse flexural test results illustrate that fiber-matrix adhesion has a stronger effect on the transverse flexural strength than on the transverse tensile strength. The authors suggested that a strong sensitivity of the ISS on the transverse flexural strength should be expected. Because the bending stresses are directly borne by the interface and the specimen failure occurs either due to tensile (or compressive) failure of the interface or matrix or a combination of the two.

Table 12 Summary of an On-Axis Property Result for Carbon/Epoxy Composite

Test	AU4/epoxy	AS4/epoxy	AS4C/epoxy
[O] ₁₂ tensile modulus, E_{11} (GPa)	130 ± 9	138 ± 5	150 ± 9
[O] ₁₂ tensile strength, σ'_t (MPa)	1403 ± 107	1890 ± 143	2044 ± 256
[O] ₁₂ compressive modulus, E_{1c} (GPa)	131 ± 8	126 ± 9	153 ± 8
[O] ₁₂ compressive strength, σ'_{1c} (MPa)	679 ± 116	911 ± 180	1174 ± 207
[O] ₁₂ three-point flexural modulus, E_{1B} (GPa)	154 ± 6	136 ± 11	147 ± 5
[O] ₁₂ three-point flexural strength, σ'_{1B} (MPa)	1662 ± 92	1557 ± 102	1827 ± 52

Source: from ref. 128. (Reprinted with permission from Chapman & Hall).

Table 13 Summary of Off-Axis Property Results for Carbon Fiber/Epoxy Composites

Measurement	AU4/epoxy	AS4/epoxy	AS4C/epoxy
[90] ₁₂ tensile modulus, E_{22} (GPa)	8.9 ± 0.6	9.8 ± 0.6	10.3 ± 0.6
[90] ₁₂ tensile strength, σ'_t (MPa)	18.0 ± 3.9	34.2 ± 6.2	41.2 ± 4.7
[90] ₁₂ flexural modulus, E_{2B} (GPa)	10.2 ± 1.5	9.9 ± 0.5	10.7 ± 0.6
[90] ₁₂ flexural strength, σ'_{2B} (MPa)	21.4 ± 5.8	50.2 ± 3.4	75.6 ± 14.0
[±45] ₁₂ in-plane shear modulus, G_{12} (GPa)	9.1 ± 1.5	6.2 ± 0.5	6.0 ± 0.2
[±45] ₁₂ in-plane shear strength, τ'_{12} (MPa)	37.2 ± 1.8	72.2 ± 12.4	97.5 ± 7.4
losipescu in-plane shear modulus, G_{12} (GPa)	7.2 ± 0.5	6.4 ± 1.0	7.9 ± 0.4
losipescu in-plane shear strength, τ'_{12} (MPa)	55.0 ± 3.0	95.6 ± 5.1	93.8 ± 3.3
Short-beam interlaminar shear strength, τ'_{13} (MPa)	47.5 ± 5.4	84.0 ± 7.0	93.2 ± 3.8

Source: from ref. 128. (Reprinted with permission from Chapman & Hall.)

Several other investigators [38,129,130] carried out detailed studies of the influence of various surface oxidation on the mechanical properties of carbon fiber-reinforced polymer (CFRP) composites. They estimated the carbon fiber composition, the amount of oxygen-containing functional groups, and surface areas of carbon fibers by measuring the content of two types of surface groups (Table 14): (1) strongly acidic groups such as carboxylic and phenolic, which could be neutralized by sodium hydroxide; and (2) weakly acidic groups (hydroxyl), neutralized by sodium ethoxide. The tensile failure mode of the composite is determined by the presence of strong acidic groups, which is indicative of a strong interfacial bond. Introduction of weak acidic groups enhanced the ILSS without a considerable alternation of the mode of failure. In other words, the nature of the interfacial bond remains almost unaltered. To examine the effect of surface groups more closely, these workers degassed oxidized carbon fibers by heat treatment in argon at 1000°C. This heat treatment removed the acidic groups almost completely. ILSS studies of the composites prepared by using these carbon fibers showed a slight decrease, although the values remained much higher than in the case of the untreated fibers. This clearly indicates that the presence of acid groups on carbon fibers strongly influenced the shear strength of the resulting composites.

To differentiate between the influence of increased surface area and increased surface functionality of the oxidized carbon fibers on the

improvement in ILSS Fitzer and co-workers [131] selected a carbon fiber (Torayca 300) which does not undergo any marked change in surface area on surface oxidation or during subsequent heat treatment. The commercial finish of the carbon fiber was removed by extraction in boiling acetone for several days followed washing with boiling water. The carbon-oxygen surface compounds formed during oxidation were removed by gradual heating between 500 and 1400°C. The surface oxides decomposed into CO₂ and CO. In addition methane was also evolved. The CO₂ was evolved mainly between 300 and 850°C, while CO was evolved largely between 350 and 1000°C. The amount of gases evolved were different for untreated (T300 U) and surface-oxidized (T300 S) samples (Table 15). The surface treated carbon fiber composites showed higher ILSS values than those of untreated fiber composites. When surface-treated carbon fiber was heated at gradually increasing temperatures, the ILSS of the fiber-composite decreased. The decrease in ILSS occurred mainly on heat treatment in the temperature range 300–450°C (Figure 37), which can be correlated directly with the removal of the surface oxides which evolve CO₂ on heating. Only a small decrease in ILSS occurred in the temperature range 500–1000°C, where most of the carbon monoxide is evolved, indicating that CO-evolving surface oxygen groups have only a minor effect on ILSS. A drastic decrease in the ILSS of the composite occurred when the carbon fibers, treated as well as untreated, were heated at temperatures above 1000°C. This decrease in ILSS at high HTT values was found to be related directly to the elimination of nitrogen from the carbon fiber samples as shown in Figure 37.

Table 14 Composite Properties in Relation to Surface Acidic Groups on Carbon Fibers

Fiber ^a	Surface group neutralized by group			ILSS	Failure mode
	NaOH ($\mu\text{Eq/g}$)	NaOC ₂ H ₅ ($\mu\text{Eq/g}$)			
AC nontreated	7	10	55		shear
AC HNO ₃	14	20	85		intermediate
AC HNO ₃ h.t.	0	15	77		intermediate
AC NaOH	16	16	92		tensile
AC NaOH h.t.	0	13	77		intermediate
AG nontreated	3	2	14		shear
AG NaOH	16	17	50		tensile
AG NaOH h.t.	2	21	51		intermediate

^ah.t., heat-treated; AC, heat-treated at temperatures below 1500°C; AG, heat-treated at 2000°C.

Source: from ref. 130.

Table 15 Amount of Desorbed Gases CO₂, CO, and CH₄ During Heat Treatment of HT Carbon Fiber T300 up to Final Temperature, Fiber Nitrogen Content, and Resulting ILSS

Fiber type	Desorption treatment (°C)	Desorbed gases ($\mu\text{mol/g}$)			Fiber analysis nitrogen (%)	Adhesion in LY556 ILSS (MPa)
		CO ₂	CO	CH ₄		
T300 U	Nil	—	—	—	—	78.6
	1000	5.16	5.93	2.76	5.6	78.7
T300 S	—	—	—	—	—	91.9
	930	11.01	5.12	1.97	—	82.0
	1000	17.69	12.53	4.59	5.4	78.9
	1200	17.50	12.82	4.92	2.6	63.5
	1400	17.82	13.91	3.97	1.1	32.6

Source: from ref. 131.

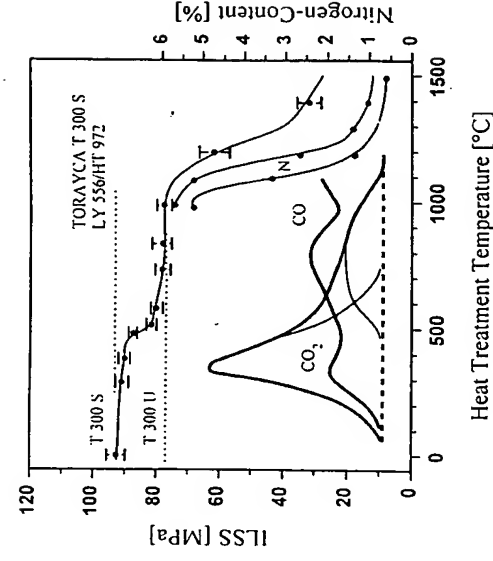


Figure 37 Relationship between ILSS and gases desorbed from carbon fiber surface [132].

ENGINEERED INTERFACES IN FIBER REINFORCED COMPOSITES

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3.3. Interlaminar/intralaminar properties

3.3.1. Introduction

In addition to the direct measurements of fiber-matrix interface properties discussed in Section 3.2, a number of testing techniques have been devised to assess the fiber-matrix interface bond quality by inference from the gross mechanical properties such as interlaminar shear strength (ILSS), translaminar or in-plane shear strength, and transverse tensile strength. These testing techniques invariably employ

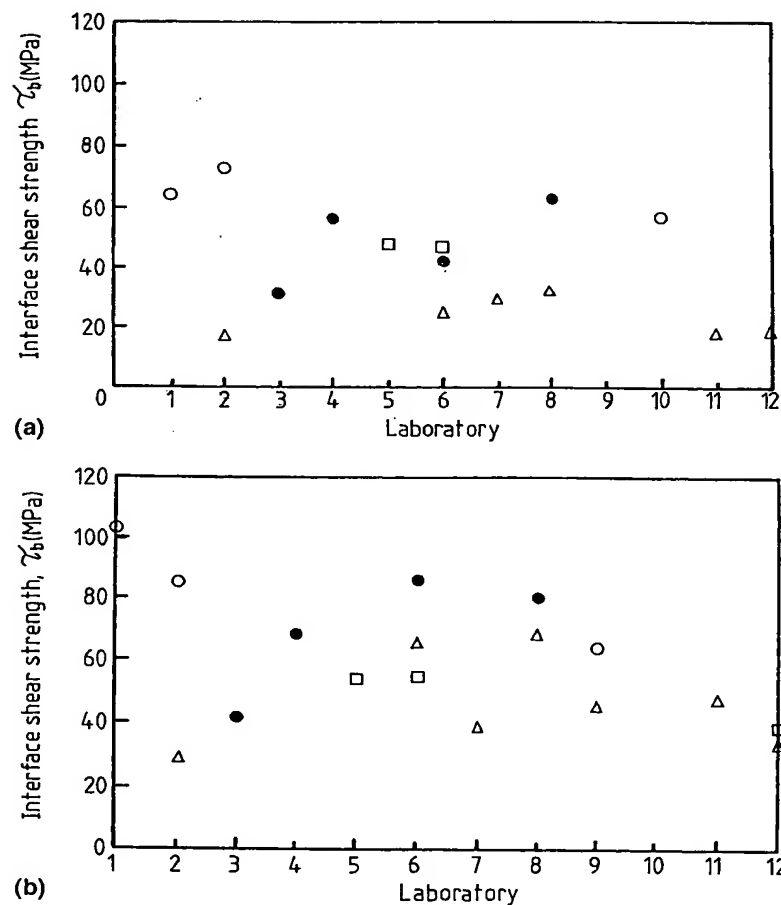


Fig. 3.15. Interface shear strength, τ_b , of (a) untreated and (b) treated LXA500 carbon fiber-epoxy matrix system measured at 10 different laboratories and using different testing methods. (○) fiber pull-out test; (●) microbond test; (□) fiber push-out test; (△) fiber fragmentation test. After Pitkethly et al. (1993).

Table 3.1

Collated data obtained from all laboratories in a round robin test programme^a

Testing method	Pull-out		Microdebond		Fragmentation		Push-out	
Fiber treatment	None	Std.	None	Std.	None	Std.	None	Std.
No. of laboratories	3	3	4	4	6	7	2	3
ISS, τ_a (MPa)	64.6	84.1	48.3	69.7	23.8	47.3	47.8	49.5
SD	8.2	19.4	14.1	19.7	6.6	15.4	0.5	9.1
CV (%)	13	23	29	28	28	33	1	18.9

Std., standard surface treatment; ISS, interfacial shear strength; SD, one standard deviation; CV, coefficient of variation.

^aAfter Pitkethly et al. (1993).

laminated composites reinforced with continuous and long fibers, whether unidirectional or cross-plyed.

Apart from the short beam shear test, which measures the interlaminar shear properties, many different specimen geometry and loading configurations are available in the literature for the translaminar or in-plane strength measurements. These include the Iosipescu shear test, the $[\pm 45^\circ]_S$ tensile test, the $[10^\circ]$ off-axis tensile test, the rail-shear tests, the cross-beam sandwich test and the thin-walled tube torsion test. Since the state of shear stress in the test areas of the specimens is seldom pure or uniform in most of these techniques, the results obtained are likely to be inconsistent. In addition to the above shear tests, the transverse tension test is another simple popular method to assess the bond quality of bulk composites. Some of these methods are more widely used than others due to their simplicity in specimen preparation and data reduction methodology.

Testing on bulk composite materials has a more serious limitation than in microcomposite tests in that the actual locus and modes of failure have to be consistent with what are originally designed for the composite in order for a specific test to be valid. Judgment of validity of the test by examining the onset of failure during the experiment is a tedious task, which cannot be assumed to have taken place for a given loading condition. Even in an apparent interlaminar shear failure, the failure may occur at the fiber-matrix interface, in the matrix or in a combination of these, depending on the loading direction relative to the interface concerned and, more importantly, on the relative magnitudes of the fiber-matrix interface bond strength and the shear strength of the matrix material. This makes the interpretation of experimental data more complicated since this requires proper micromechanics analysis to be developed together with prior knowledge of the matrix properties (Lee and Munro, 1986; Pindera et al., 1987).

3.3.2. Short beam shear test

The short beam shear test designated in ASTM D 2344 (1989) involves loading a beam fabricated from unidirectional laminate composites in three-point bending as

illustrated in Fig 3.16. In interpreting the short beam shear test, the maximum value τ_{\max} (i.e. the ILSS of the shear stress distribution along the thickness direction, is related to the maximum applied load P_{\max} , and specimen width b and thickness t , according to the classic short beam shear relationship

$$\tau_{\max} = \frac{3P_{\max}}{4bt} \quad (3.10)$$

It is easily seen that even in the absence of any substantial bonding at the fiber-matrix interface, ILSS of the composite laminate still has a lower-bound value which is contributed solely by the shear strength of the matrix τ_m . For a brittle matrix beam with cylindrical pores (in place of the fibers of volume fraction V_f in square array), the lower bound ILSS can be estimated from $\tau_m[1 - (4V_f/\pi)^{1/2}]$, which depends strongly on the fiber V_f . This implies that the ILSS cannot be regarded as giving the genuine values of the bond strength. Nevertheless, because of the simplicity of the test method and minimum complication in specimen preparation, the short beam shear test has become one of the most popular methods to determine the interlaminar bond quality of composites containing both polymer and metal matrices. It has been most widely used to assess the effects of fiber finish and surface treatments, fiber-matrix compatibility for the development of new fiber or matrix systems, etc.

This test has an inherent problem associated with the stress concentration and the non-linear plastic deformation induced by the loading nose of small diameter. This is schematically illustrated in Fig 3.17, where the effects of stress concentration in a thin specimen are compared with those in a thick specimen. Both specimens have the same span-to-depth ratio (SDR). The stress state is much more complex than the pure shear stress state predicted by the simple beam theory (Berg et al., 1972;

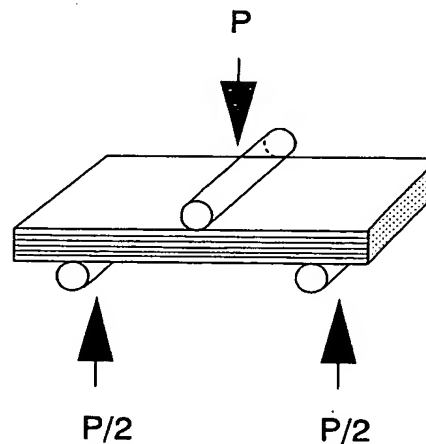


Fig. 3.16. Schematic of loading configuration of short beam shear test.

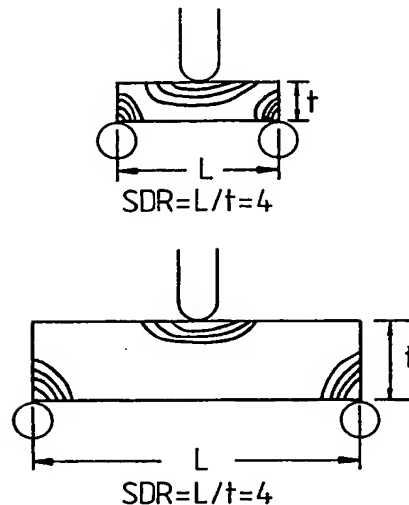


Fig. 3.17. Effect of stress concentrations on short beam shear specimens: (a) thin specimen; (b) thick specimen. After Browning et al. (1983).

Sandorf, 1980; Whitney, 1985; Whitney and Browning, 1985). According to the classical beam theory, the shear stress distribution along the thickness of the specimen is a parabolic function that is symmetrical about the neutral axis where it is at its maximum and decreases toward zero at the compressive and tensile faces. In reality, however, the stress field is dominated by the stress concentration near the loading nose, which completely destroys the parabolic shear distribution used to calculate the apparent ILSS, as illustrated in Fig 3.18. The stress concentration is even more pronounced with a smaller radius of the loading nose (Cui and Wisnom, 1992) and for non-linear materials displaying substantial plastic deformation, such as Kevlar fiber-epoxy matrix composites (Davidovitz et al., 1984; Fisher et al., 1986), which require an elasto-plastic analysis (Fisher and Marom, 1984) to interpret the experimental results properly.

The high stress concentration and damage by crushing in severe cases at the loading nose with a very small SDR may induce premature failure in the compressive face before interlaminar failure (Fig 3.19) (Berg et al., 1972; Whitney and Browning, 1985). This problem causes a significant limitation in relation to the failure mode transition depending on the SDR. It is well known that flexure specimens, which normally fail in the shear mode, may fail under compression with the increase in the SDR above a critical value (Sattar and Kellogg, 1969; Fisher et al., 1986). The critical SDR in general increases with large fiber volume fraction, V_f , and weakened interface bonding for a given fiber-matrix composite (Shih and Ebert, 1986; Birger et al., 1989). This failure mode transition behavior is very sensitive to the loading rate (Boukhili et al., 1991). Non-shear or mixed mode failure can result in invalid data with the calculated ILSS being too high with respect to the flexural

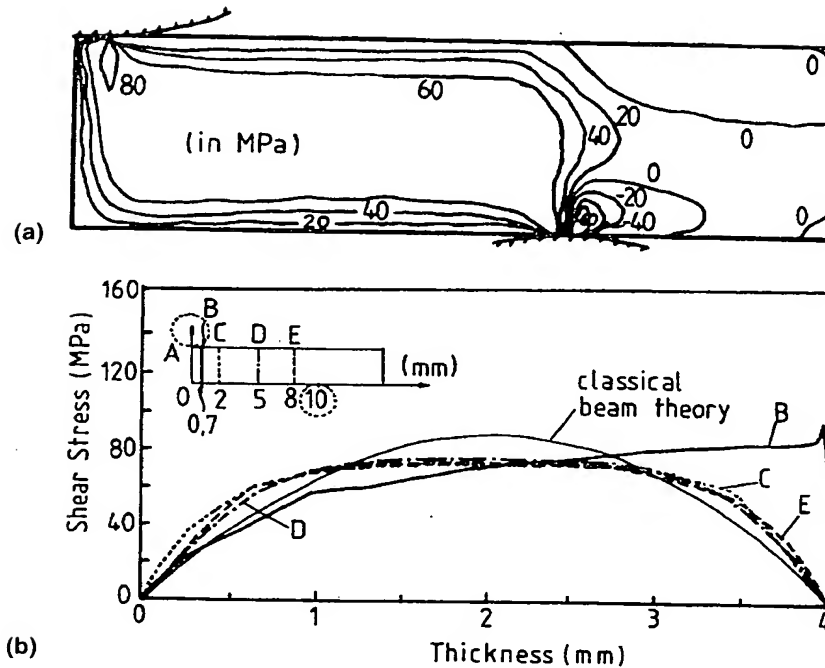


Fig. 3.18. (a) Shear stress contours and (b) shear stress distributions across the thickness of a three-point bending specimen in a short beam shear test. After Cui and Wisnom (1992). Reproduced by permission of Elsevier Science Ltd.

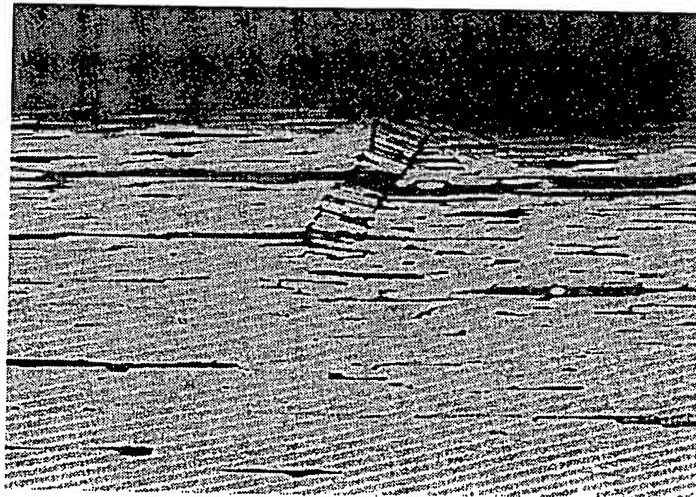


Fig. 3.19. Scanning electron microphotograph of buckling failure near the loading nose of a carbon fiber-epoxy matrix short beam shear specimen. After Whitney and Browning (1985).

strength. Therefore, in-situ microscopic examination is often necessary to ensure that interlaminar shear failure occurs at the maximum bending load.

Since the range of SDR that consistently produces interlaminar shear failure is very small (i.e. four or five when the Young's moduli for the composites are greater or less than 100 GPa, respectively, in accordance with the specification (ASTM D 2344, 1989)), the specimen has to be very thick, which is both expensive and more difficult to fabricate. As an alternative, four-point bending of a long thin specimen is suggested (Browning et al., 1983), whereby the sharing of the total load between two loading noses can reduce the local stress concentration compared to three-point bending (Cui and Wisnom, 1992).

3.3.3. Iosipescu shear test

The Iosipescu shear test (Iosipescu, 1967) is an ideal method that is relatively simple to conduct with small and easily fabricated specimens, and it is capable of measuring reliable shear strength and the modulus simultaneously (Lee and Munro, 1990). This test employs a double-edge notched specimen that is subjected to two counteracting moments produced by force couples as shown in Fig 3.20(a). In a qualitative photoelastic study, Iosipescu (1967) showed that when the depth of each 90° vee-notch is between 20% and 25% (typically 22%) of specimen depth and the notch tip radius is zero (i.e., a sharp notch), the stress state across the notched section is under pure and uniform shear for an isotropic material. This is a direct result from the coincidence between the directions of the principle stresses at $\pm 45^\circ$ to the specimen axis and the 90° notch angle in the region of the zero bending moment. In this case, there is no stress singularity at the notch tip because of the absence of normal stresses at the point. The average shear stress in the middle section of the specimen with width b is simply given by the applied load P , divided by the net cross-sectional area

$$\tau = \frac{P}{bt} \quad (3.11)$$

To calculate the shear modulus, strain gauges are used to obtain the shear stress-shear strain curve. Attracted by the almost pure shear state generated at the test section, a number of researchers have studied the applicability of this test technique to advanced composite materials, using FEMs as well as other experimental means. Adams and Walrath (1982, 1987a, b) in particular have evaluated the shear stress distribution as a function of notch depth, angle, notch tip radius, etc., which resulted in redesigning the specimen geometry and test fixture. It is clearly shown that there is a substantial stress concentration near the notch tip and the shear stress distribution in the middle section of orthotropic specimen is not uniform as opposed to isotropic materials. The stress concentration is found to be a function of the orthotropic ratio (i.e., Young's moduli ratio between two principal in-plane directions, E_{11}/E_{22} , which is governed by the fiber orientation and the fiber volume fraction) and notch geometry, and can be reduced by incorporating a large notch tip radius with a large